Evaluation of Regenerative Activated Carbon Catalysts

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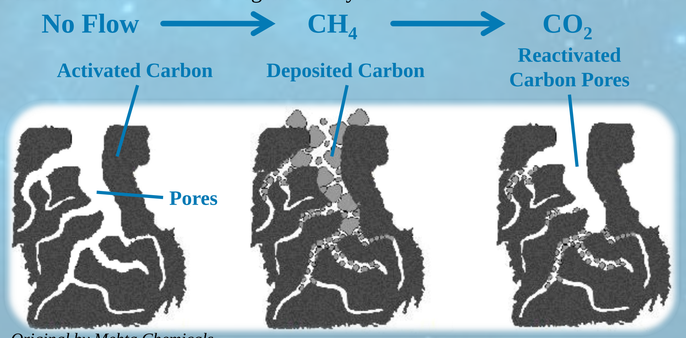
Introduction

Maximum oxygen recovery is essential for long-term manned exploration missions. State-of-the-art Sabatier technology only recovers 50% oxygen from metabolic carbon dioxide. However, hydrogen recovered with a Sabatier post-processor can be used to theoretically achieve 100% oxygen recovery. One potential post-processor technology of interest is methane pyrolysis.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \text{Sabatier Reaction}$$
$$CH_4 \rightarrow C(s) + 2H_2 \qquad \text{Methane Pyrolyis}$$

Most catalytic methane pyrolysis technologies face catalyst deactivation due to carbon deposition on the catalyst. This deactivation necessitates research on regenerative catalysts capable of mitigating unwanted carbon build-up on catalyst surfaces. One potential regenerative catalyst is activated carbon. Activated carbons are high-porosity carbons with large surface areas making them ideal for catalysis. Additionally, carbon formed on the surface can be re-activated. Thus, the carbon product becomes the catalyst. The carbon becomes "re-activated" by increasing its surface area when oxygen from added carbon dioxide extracts some of the carbon out of its solid state to form carbon monoxide. This creates pores in the carbon, thus creating an "activated carbon." The objective of the current investigation was to identify the deactivation curve and regenerability of five activated carbons.



Original by Mehta Chemicals

The regeneration reaction is the reverse Boudouard shown below.

$$CO_2 + C(s) \rightarrow 2CO \qquad \text{Reverse Boudouard}$$

Methodology

Five trials of deactivation and regeneration were conducted on five activated carbons (described below) in the Bosch Catalyst Test Stand (B-CaTS) and a micro gas chromatograph (µGC) was used to analyze the system composition.

B-CaTS Furnace and Reactor

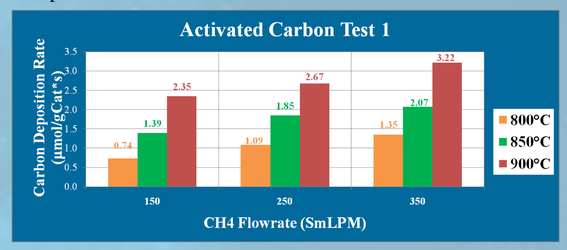
- Deactivation parameters include 900°C, 15psia, and a 15.625 mmol per min CH_4 feed rate
- Regeneration parameters include 900°C, 15psia, and an 11.16 mmol per min CO_2 feed rate

Activated Carbon	Surface Area (m^2/g)	Grain Size (mm)
1. NORIT GAC 1240 PLUS	900-950	0.42-2.00
2. NORIT GAC 830 PLUS	900-950	0.42-2.36
3. DARCO 4X12	600-650	1.70-4.75
4. DARCO 12X20	600-650	0.85-1.70
5. DARCO 20X40	600-650	0.42-0.85

Results and Discussion

Initial Study

To determine the deactivation parameters, an initial study was conducted using NORIT GAC 1240 PLUS at three flow rates and three temperatures shown in the graph below. It was concluded that a 900°C temperature and 350 SmLPM (15.625 mmol per minute) CH_4 flow rate lead to the greatest carbon deposition.



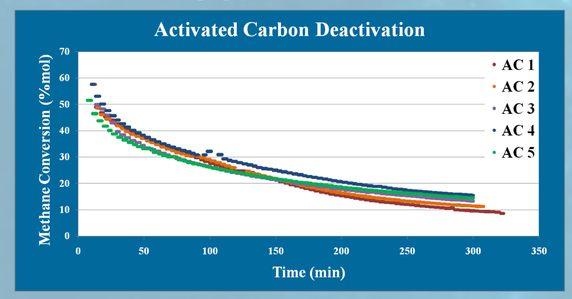
Deactivation

Each activated carbon was deactivated for five hours to determine performance. The effects of deactivation on the tube for a single trial are shown right. Carbon deposited on the catalyst as expected; however, carbon was observed on the tube as well. Although unproven, this carbon is believed to be a product of "delayed coking," in which free radicals cause the reaction to proceed downstream of the catalyst.

DARCO 4X12 Before Deactivation

DARCO 4X12 After Deactivation

The level of deactivation was measured by a change in methane conversion. Each of the activated carbons showed similar initial performance with methane conversion between 50-60%. Similarly, all activated carbons had very comparable deactivation rates with less than 20% methane conversion at the end of the five hour test period, as shown in the deactivation graph below.



The similar deactivation curves above suggest that the type, grain size, and surface areas had an insignificant effect on overall deactivation. Different grain sizes (as shown in the examples to the right) were expected to result in dissimilar deactivation rates due to different total available surface area, but this was not observed in testing. It is probable that mass transport of methane to the catalyst surfaces and into and out of pores was the limiting factor in these tests. If the system had been operated at kinetically limiting conditions, a greater variation in deactivation rates would have been observed.

DARCO 20X40

DARCO 4X12

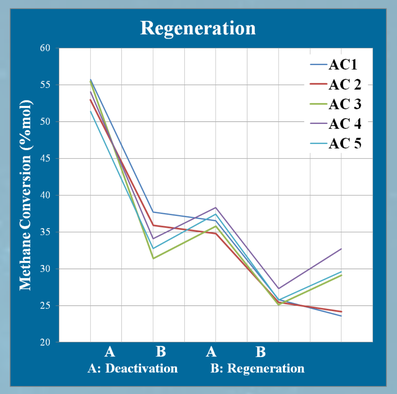
Regeneration

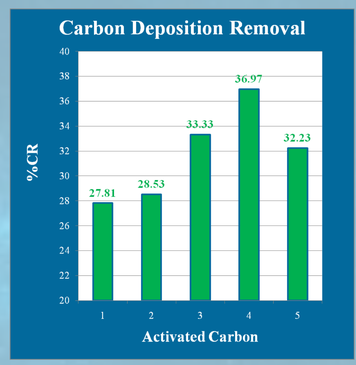
Regeneration Procedure

Deactivation → Regeneration → Deactivation → Regeneration → Deactivation

Note: Each deactivation or regeneration period is 1 hour in length.

- The graph (right) shows the change in methane conversion observed during deactivation and regeneration for each activated carbon.
- Unlike the deactivation results, there is a noticeable correlation between catalyst type and regenerability.
- The lower surface area carbons were more regenerable possibly because carbon is more easily removed from larger pores than small ones.





- The percent of carbon removed, shown in the graph (left) is calculated as follows:

$$\%CR = 100 * \frac{m_{CR}}{m_{CD}}$$

where *CD* is carbon deposited, *CR* is carbon removed and *m* is mass.

- Corresponding with the graph above, activated carbons 3, 4, and 5 showed more carbon removal than activated carbons 1 and 2.

Conclusion

The activated carbons explored in this study showed significant potential as methane pyrolysis catalysts as observed in deactivation testing. However, they do not currently meet the regenerability requirements necessary for an oxygen-recovery system. This data refutes the literature which claims nearly complete regeneration of activated carbons with carbon dioxide.

Future Work

- Perform regeneration with either steam or a carbon dioxide-steam combination for surface gasification
- Test different regeneration flow rates, times, and temperatures to maximize regeneration
- Explore other activated carbons

References

[1] "Thermocatalytic Decomposition of Methane over Carbon-based Catalysts" presented by Dr. Nazim Muradov of the Florida Solar Energy Center at the 2009 Atmosphere Revitalization Loop Closure Technical Interchange Meeting, held August 15-17, 2009 at MSFC.

[2] "Catalytic activity of carbons for methane decomposition reaction" from Catalysis Today (2005, volume 102-103, pgs. 225-233) written by Nazim Muradov, Franklyn Smith, and Ali T-Raissi.

[3] "Autothermal Catalytic pyrolysis of methane as a new route to hydrogen production with reduced CO2 emissions" from Catalysis Today (2006, volume 116, pgs. 281-288) written by Nazim Muradov, Franklyn Smith, Cunping Huang, and Ali T-Raissi.